



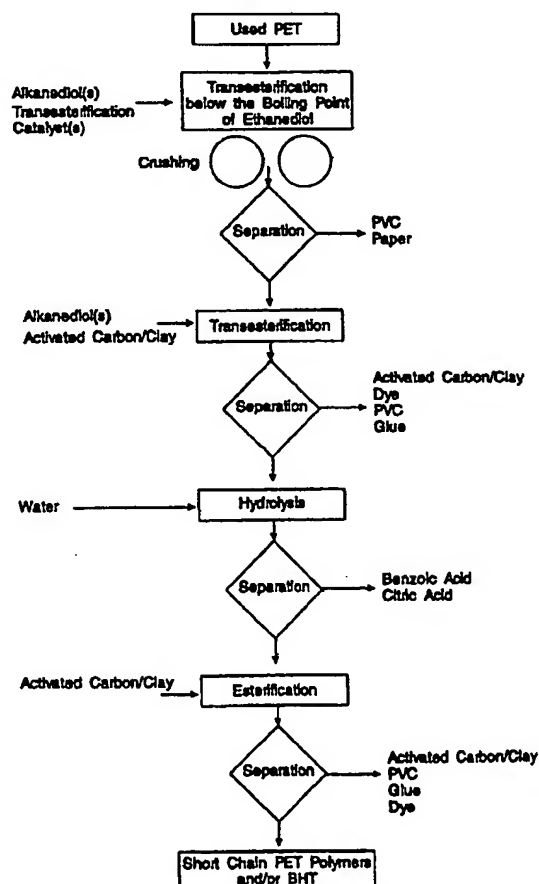
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: IMPROVED POLYETHYLENE TEREPHTHALATE DECONTAMINATION

## (57) Abstract

A process for removing contaminants from polyethylene terephthalate ("PET") components by depolymerising PET including transesterifying material containing PET by reacting an alkanediol or alkanediols at a temperature below the boiling point of ethanediol with the material for a predetermined period of time to form a mixture containing embrittled PET; crushing the mixture and separating uncrushed material from the crushed material which contains PET; transesterifying the crushed PET by reacting an alkanediol or alkanediols at a temperature between at or about the boiling point of ethanediol and 240 degrees Celsius with the recovered PET for a predetermined period of time to form a solution containing soluble short chain PET polymers and/or bis (hydroxy ethyl) terephthalate ester ("BHT"); recovering short chain PET polymers and/or BHT and ethanediol; and hydrolysing the recovered short chain PET polymers and/or BHT at elevated pressure and temperature for a predetermined period of time to form an ethanediol solution and crystals of terephthalic acid.



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## IMPROVED POLYETHYLENE TEREPHTHALATE DECONTAMINATION

### FIELD OF THE INVENTION

The present invention relates to a method for the decontamination of polyethylene terephthalate ("PET") components at reduced temperature. The invention also proposes a method for separating PET components from other materials.

### BACKGROUND TO THE INVENTION

PET is a thermoplastic polyester that can be formed from 1:2 ethanediol and terephthalic acid by direct esterification to form bis (hydroxy ethyl) terephthalate ester ("BHT") which is then polymerised by catalysed ester exchange to useful polymers.

Traditionally, PET has been used extensively because it can be offered as an oriented film or fibre, has high tenacity, good electrical resistance and low moisture absorption together with a melting point of approximately 265 degrees Celsius.

For these reasons, its uses have been very diverse extending from being blended with cotton for wash and wear fabrics, blended with wool for worsteds and suitings, packaging films and recording tapes and containers including soft drink containers.

There are a number of applications of PET where remelting and reforming is not permissible or gives inferior properties. The reuse of PET for those applications is best achieved by degrading the polymer into the original monomers namely ethanediol and terephthalic acid then reacting the monomers together to regenerate the original PET.

In International Patent Application No. PCT/AU93/00198 a process is disclosed in which PET is made brittle by partial transesterification as a precursor to crushing and separation of the crushed material, which contains PET, from other substances. These other substances, for example, paper and poly vinyl chloride ("PVC") remain ductile, enabling the separation of non-PET substances by crushing and screening. According to the invention disclosed in the patent application, the embrittlement of PET by partial transesterification is carried out by mixing ethanediol (or alkanediols other than ethanediol) having a temperature at or about the boiling point of ethanediol with the material for a predetermined period of time.

While the invention disclosed in Patent Application No. PCT/AU93/00198 represents a significant advance in the decontamination of PET-containing substances, subsequent investigations have revealed that at or about the atmospheric boiling point of ethanediol, the non-PET substances, such as paper and PVC, may be adversely affected. PVC, in particular, may be chemically degraded in such a way as to alter its ability to be

commercially recovered. For example, at or about the boiling point of ethanediol PVC is severely degraded as it is dehydrochlorinated which yields a brown brittle product. The resultant brown product is not suitable for re-extrusion to make commercially useful recycled products.

- 5 Consequently, further investigation have been directed towards the process of PET decontamination with the view of balancing the need for adequate embrittlement of PET whilst avoiding unwanted degradation of non-PET components.

### SUMMARY OF THE INVENTION

- 10 Surprisingly it has now been found that satisfactory levels of embrittlement of PET components can be achieved at temperatures below the boiling point of ethanediol. As non-PET components are less susceptible to degradation at these lower temperatures, it is now possible to partially transesterify PET without adversely affecting those other components.

Thus, according to the present invention, a process is provided for removing contaminants from PET components by depolymerising PET, including the following steps:

- 15 (a) transesterifying material containing PET by reacting an alkanediol or alkanediols at a temperature below the boiling point of ethanediol with the material for a predetermined period of time to form a mixture containing embrittled PET;
- (b) crushing the mixture and separating uncrushed material from the crushed material which contains PET;
- 20 (c) transesterifying the crushed PET by reacting an alkanediol or alkanediols at a temperature between at or about the boiling point of ethanediol and 240 degrees Celsius with the recovered PET for a predetermined period of time to form a solution containing soluble short chain PET polymers and/or BHT;
- (d) recovering short chain PET polymers and/or BHT and ethanediol; and
- 25 (e) hydrolysing the recovered short chain PET polymers and/or BHT at elevated pressure and temperature for a predetermined period of time to form an ethanediol solution and crystals of terephthalic acid.

The invention further provides a process for removing contaminants from PET components by depolymerising PET, including the following steps:

- 30 (a) transesterifying material containing PET by reacting an alkanediol or alkanediols at a temperature below the boiling point of ethanediol with the material for a predetermined period of time to form a mixture containing embrittled PET;
- (b) crushing the mixture and separating uncrushed material from the crushed material which contains PET;

- (c) hydrolysing the crushed PET at elevated pressure and temperature for a predetermined period of time to form an ethanediol solution and crystals of terephthalic acid;
- (d) esterifying the ethanediol solution and crystals of terephthalic acid to form short chain PET polymers and/or BHT; and
- (e) recovering short chain PET polymers and/or BHT from the mixture.

The invention further provides a process for separating PET components from other materials, including the following steps:

- (a) transesterifying material containing PET by reacting an alkanediol or alkanediols at a temperature below the boiling point of ethanediol with the material for a predetermined period of time to form a mixture containing embrittled PET; and
- (b) crushing the mixture and separating uncrushed material from the crushed material which contains PET.

In preferred forms of the invention, the alkanediol or alkanediols are selected from the group including ethanediol, 1:4 butanediol and 1:6 hexanediol and mixtures thereof. Ethanediol is particularly preferable as it is one of the monomers used in the direct esterification to form PET. The use of alkanediols other than ethanediol therefore introduces into the reaction a substance which must ultimately be separated.

The temperature of the alkanediol or alkanediols used in steps (a) above in the transesterification of the PET component is preferably in the range of 130 degrees Celsius to within 10 degrees Celsius of the boiling point of ethanediol and is particularly preferred to be in the range of 140 degrees Celsius to 160 degrees Celsius. This latter temperature range is preferred when separation of PVC or other non-PET components is desired for re-use. This will significantly avoid degradation of PVC by dehydrochlorination which poses problems with the re-use of PVC. The release of hydrogen chloride in the reactor is also substantially eliminated.

The predetermined time for embrittlement may commercially lie in the range of up to 150 minutes although, of course, longer times may still achieve the desired level of embrittlement of PET without adverse effect upon contaminants. In a preferred form of the invention, embrittlement is caused to occur within a period of between 30 minutes and 120 minutes and more preferably, between 45 minutes and 60 minutes. The transesterification giving embrittlement is preferably controlled by both temperature and time to give a brittle product with minimum over treatment. This can be effected by using plug flow reactors with a narrow range of residence times. However, if the residence time is not critical to the cost of the process then there is no technical limitation on residence time. It is anticipated

that most process designers will select a residence time between 45 and 60 minutes to enable the use of a smaller sized plant. The use of a time of more than 45 minutes also substantially ensures only a small range in the residence times, so giving a small range in the degree of brittleness of PET.

- 5 It is known that the production of PET from BHT can be improved by using a wide range of transesterification catalysts. For example, United States Patent No. 2 534 028, United States Patent No. 2 518 283, United States Patent No. 2 641 592, United States Patent No. 2 578 660, United States Patent No. 2 643 989, United States Patent No. 2 662 093, United States Patent No. 2 647 885 and United States Patent No. 2 491 660 describe methods for  
10 using suitable catalysts. Typically it is common to employ antimony (III) oxide, antimony (III) acetate and germanium dioxide as the catalyst in the esterification of PET.

- Surprisingly, it has also been found that the addition of transesterification catalysts to the alkanediol or alkanediols further reduces the temperature or time necessary to achieve the required embrittlement. This is particularly useful if the time for embrittlement is  
15 uneconomical and the addition of catalyst can reduce the time to an economic residence time. Alternatively, the reduced reaction temperature can be valuable if a reduced vapour pressure of ethanediol is to be used, or temperatures which degrade other useful substances mixed with PET are to be avoided. The addition of catalyst to the mixture for transesterification, supplements the small pre-existing concentration of catalyst in the feed  
20 stock PET, residual from the original polymerisation.

- Preferably, the transesterification catalyst may be the known useful transesterification catalysts selected from the group including antimony (III) oxide, antimony (III) acetate, germanium dioxide, manganese acetate, tetra butoxy titanium and mixtures thereof. Those skilled in the art would understand that any of the known transesterification catalysts  
25 would have a similar action, but may be less acceptable to consumers as coloured by-products are generated by the other disclosed catalysts.

- Embrittlement, which takes place prior to the collapse of the original PET structure allows the PET to be crushed to separate it from the contaminants. This allows separation to take place on the basis of size and density. Crushing to a diameter of less than 1 millimetre is  
30 preferred. Crushing can be achieved by rollers or hammer mills or any other known techniques for reducing the size of particles. Once crushed, the PET is separated from typical contaminants such as hydrocarbons and pigments from paper. Other substances giving rise to coloured products can be separated by screening, washing or density separation from other contaminants which have not become embrittled. A number of  
35 substances such as Nylons dissolve in the hot alkanediols and are removed with the liquid alkanediol. Preferably, the uncrushed material includes PVC.

Preferably, the temperature of the alkanediol or alkanediols in the transesterification of the crushed PET which form a solution of short chain PET polymers and BHT, is within the range of between at or about the boiling point of ethanediol (preferably within 5 or 10 degrees Celsius of the boiling point of ethanediol) and 240 degrees Celsius. In a particularly preferred form of the invention, the temperature range is between 220 degrees Celsius and 240 degrees Celsius. Again, preferably the alkanediols are selected from the group including ethanediol, 1:4 butanediol and 1:6 hexanediol and mixtures thereof. Ethanediol is most preferred.

Once solubilised, separation of the PET rich fraction in one preferred form of the invention can take place by filtration methods and more preferably by high pressure filtration methods. The addition of activated carbon or a combination of activated carbon and activated clay is used as an adsorbent for a wide variety of molecules such as dyes, pesticides, coloured polymers, etc. If alkanediols other than ethanediol have been used, they can also be removed at this time by known separation techniques.

Other foreign plastics with an alkane chain do not depolymerise in the alkanediol but only melt so that they may be removed by either flotation on the denser alkanediol (for example, ethanediol 1114 kilograms/m<sup>3</sup>) or screened from embrittled PET or the short chain PET polymer and/or BHT solution. Proteins and polyamides that do not react with alkanediol are recovered with the other plastics. Other polyesters are also transesterified and contaminate the short chain PET polymer solution.

It is to be understood that the present invention does not require that all the PET is converted to BHT but rather that the polymer chain length is sufficiently shortened so that the terephthalate containing molecules are soluble in the alkanediols to permit separation of foreign materials and rapid subsequent hydrolysis.

Following transesterification, the short chain PET polymers and/or BHT may be purified by crystallisation in water, thereby liberating excess ethanediol. The precipitate is filtered off. The filtrate containing ethanediol is recovered using known techniques of fractional distillation from the additional water (British Patent No. 610136). Water soluble impurities such as sugar and citric acid from soft drinks may be partially removed in the filtrate and rejected as an involatile residue by distilling off the ethanediol.

The short chain PET polymers and/or BHT are hydrolysed with water at elevated pressures and temperatures to give ethanediol and crystalline terephthalic acid. Typically the hydrolysis is performed by pumping the molten BHT and water at 230 degrees Celsius into a continuous reactor held at 40 bar with a small addition of 1% free terephthalic acid. The mixture reacts over a period of 10 minutes and is then released through a let down valve. The water and some ethanediol evaporate leaving a slurry of terephthalic acid crystals in

ethanediol and water. The crystals are washed with water to remove ethanediol which is recovered as described before.

A number of water soluble substances (for example, citric acid, phosphoric acid, sodium chloride and sulphuric acid) in the feed stock will be present in the mixture of terephthalic acid and ethanediol and are separated by the filtration. Additionally, a wide variety of compounds such as protein, paper, fats and some pesticides will be hydrolysed and made water soluble relative to the very insoluble terephthalic acid.

The ethanediol is readily purified by distillation and may be partially recycled to give both product for further polymerisation and enough product to react with fresh PET. Contaminant alcohols such as methanol from ethylene methyl acrylate or hexanediol from polyester are separated by distillation. Residual alkanediols used as reactants in the method can also be separated by distillation.

Where in this specification reference is made to the boiling point of ethanediol, it is taken to be 196-197 degrees Celsius.

## 15 DESCRIPTION OF THE DIAGRAM

One form of the invention is illustrated in the accompanying flow chart.

Used PET is initially subjected to transesterification with alkanediol having a temperature below the boiling point of ethanediol for a pre-determined time to embrittle PET. Additionally, a transesterification catalyst can be added to the mixture. Thereafter the mixture is passed through rollers which crush the embrittled PET.

The non-crushed (ductile) components of the mixture are separated by screening from the remainder of the mixture. The PET fines are then subjected to a further transesterification process.

Activated carbon and clay are added during transesterification to adsorb contaminants. During this further transesterification process the PET is converted into short chain PET polymers and/or BHT which are soluble.

The resultant solution is subjected to a further separation by screening and/or high pressure filtration to remove contaminants such as activated carbon, clay, dye, PVC and glue.

The filtrate is hydrolysed with water under elevated pressures and temperatures to form ethanediol and crystalline terephthalic acid. Acids (for example, benzoic and citric acids) remain in solution and are separated from crystalline terephthalic acid. It will be understood by persons skilled in that art that contamination of the short chain PET polymers and/or BHT by benzoic, adipic and sebacic acid may be rectified because the free



acids are approximately 1000 times more soluble in the wash water allowing some foreign polyester in the feed.

The ethanediol and terephthalic acid are esterified to short chain PET polymers and/or BHT. Activated carbon and activated clay are added and then any remaining contaminants  
5 for example PVC, glue and dye are removed by filtration.

### EXAMPLES

The invention will now be further illustrated by the following non-limiting examples.

The examples were all carried out at atmospheric pressure. It should be understood by those skilled in the art that the pressure should be reduced until a reaction temperature is  
10 reached to allow control of water in the reaction mixture.

#### Example 1

Ethanediol (500 ml) was heated to a temperature of 160 degrees Celsius. 100 grams of mixed PET and PVC was placed in the hot reagent for 80 minutes then recovered and crushed. The PET was readily crushed and the PVC was not discoloured and the original  
15 ductility was maintained.

#### Example 2

A solution of 2% antimony (III) oxide in ethanediol (500 ml) was prepared and held at a temperature of 160 degrees Celsius. 100 grams of mixed PET and PVC was placed in the hot reagent for 60 minutes then recovered and crushed. The PET was readily crushed and  
20 the PVC was not discoloured and the original ductility was maintained.

#### Example 3

A hot solution of 2% antimony (III) acetate in ethanediol (500 ml) was prepared. 100 grams of mixed PET and PVC was placed in the hot solution then recovered for the following temperatures and times:

- 25           160 degrees Celsius for 50 minutes;  
              150 degrees Celsius for 60 minutes; and  
              140 degrees Celsius for 120 minutes.

In each test, the PET was readily crushed and the PVC was not discoloured and the original ductility was maintained.

**Example 4**

A partial solution of 5% germanium dioxide suspension in ethanediol being a saturated solution (150 ml) was prepared and held at a temperature of 160 degrees Celsius. 15 grams of mixed PET and PVC was placed in the hot solution for 60 minutes. The mixture was readily crushed and the PVC recovered without significant degradation.

**Example 5**

The same partial solution of example 4 was prepared but held at a temperature of 130 degrees Celsius. 15 grams of mixed PET and PVC was placed in the hot solution for in excess of 210 minutes. The mixture was readily crushed and the PVC recovered without significant degradation.

**Example 6**

100 grams of mixed PET and PVC was placed in hot 1:4 butanediol then recovered for the following temperatures and times:

- 190 degrees Celsius for 50 minutes;
- 170 degrees Celsius for 120 minutes; and
- 155 degrees Celsius for 180 minutes.

In each test, the PET was readily crushed. In this example at 170 degrees Celsius and 155 degrees Celsius, the PVC was not discoloured and the original ductility was maintained.

**Example 7**

100 grams of mixed PET and PVC was placed in hot 1:6 hexanediol then recovered for the following temperatures and times:

- 190 degrees Celsius for 50 minutes;
- 170 degrees Celsius for 120 minutes; and
- 155 degrees Celsius for 180 minutes.

In each test, the PET was readily crushed. In this example at 170 degrees Celsius and 155 degrees Celsius, the PVC was not discoloured and the original ductility was maintained.

In all of the above examples, the crushed PET was screened using ethanediol as an aid then the fines passing the screen were heated for one hour to convert the PET to soluble products. A mixture of 5 grams of activated carbon and 5 grams of activated clay were added and the mixture heated and stirred for 15 minutes then filtered and the product hydrolysed to give terephthalic acid and ethanediol/water.

It can be understood from the examples that the temperature required for embrittlement can be significantly reduced from that previously disclosed as necessary for adequate embrittlement. Since at these lower temperatures, the PVC was not degraded, it could be recovered in a useful state.

- 5 Accordingly, the lower temperatures for transesterification in the present invention permits a more economical processing of a wider range of mixed feed stocks.

Since modifications to the steps described are various and obvious to those skilled in the art, it is to be understood that this invention is not limited to the particular embodiments described.

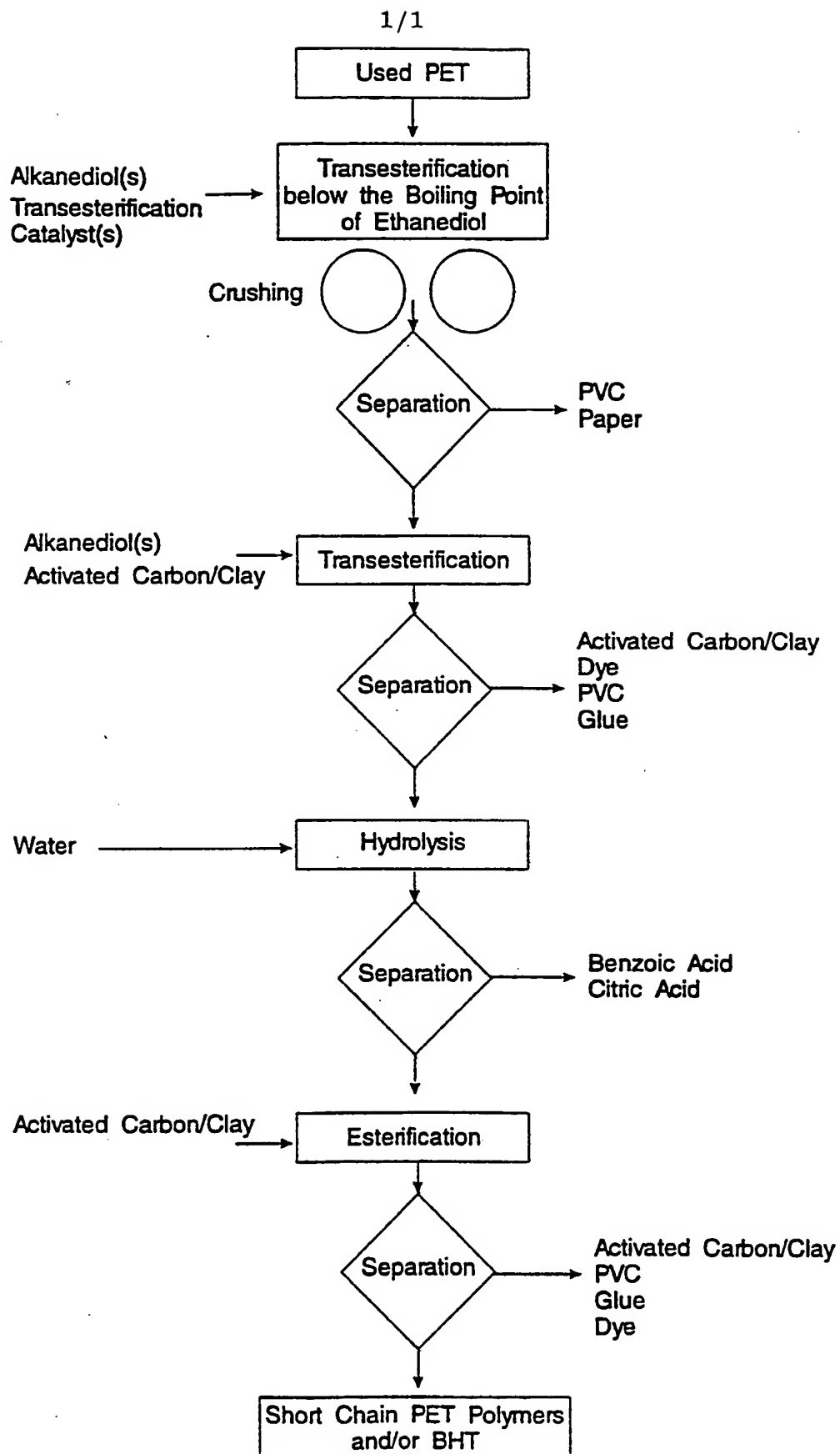
**THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:**

1. A process for removing contaminants from polyethylene terephthalate ("PET") components by depolymerising PET, including the following steps:
  - 5 (a) transesterifying material containing PET by reacting an alkanediol or alkanediols at a temperature below the boiling point of ethanediol with the material for a predetermined period of time to form a mixture containing embrittled PET;
  - (b) crushing the mixture and separating uncrushed material from the crushed material which contains PET;
  - 10 (c) transesterifying the crushed PET by reacting an alkanediol or alkanediols at a temperature between at or about the boiling point of ethanediol and 240 degrees Celsius with the recovered PET for a predetermined period of time to form a solution containing soluble short chain PET polymers and/or bis (hydroxy ethyl) terephthalate ester ("BHT");
  - 15 (d) recovering short chain PET polymers and/or BHT and ethanediol; and
  - (e) hydrolysing the recovered short chain PET polymers and/or BHT at elevated pressure and temperature for a predetermined period of time to form an ethanediol solution and crystals of terephthalic acid.
- 20 2. The process of claim 1, wherein the alkanediol or alkanediols are selected from the group including ethanediol, 1:4 butanediol and 1:6 hexanediol and mixtures thereof.
3. The process of claim 1, wherein the alkanediol is ethanediol.
4. The process of any one of claims 1 to 3, wherein step (a) is carried out at a temperature in the range of between 130 degrees Celsius and within 10 degrees  
25 Celsius of the boiling point of ethanediol.
5. The process of any one of claims 1 to 3, wherein step (a) is carried out at a temperature in the range of between 140 degrees Celsius and 160 degrees Celsius.
6. The process of any one of claims 1 to 5, wherein the uncrushed material includes poly vinyl chloride.
- 30 7. The process of any one of claims 1 to 6, wherein the predetermined period of time in step (a) is between 30 minutes and 120 minutes.
8. The process of any one of claims 1 to 6, wherein the predetermined period of time in step (a) is between 45 minutes and 60 minutes.

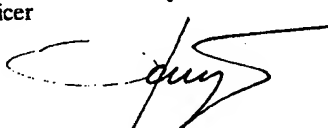
9. The process of any one of claims 1 to 8, wherein step (a) further includes the addition of a transesterification catalyst.
10. The process of claim 9, wherein the transesterification catalyst is selected from the group including antimony (III) oxide, antimony (III) acetate, germanium dioxide, manganese acetate, tetra butoxy titanium and mixtures thereof.
11. The process of any one of claims 1 to 10, wherein the PET is crushed to a size of less than 1 millimetre.
12. The process of any one of claims 1 to 11, wherein in step (c) the range is between a temperature within 10 degrees Celsius of the boiling point of ethanediol and 240 degrees Celsius.
13. The process of any one of claims 1 to 11, wherein in step (c) the range is between a temperature within 5 degrees Celsius of the boiling point of ethanediol and 240 degrees Celsius.
14. The process of any one of claims 1 to 11, wherein step (c) is carried out at a temperature of between 220 degrees Celsius and 240 degrees Celsius.
15. The process of any one of claims 1 to 14, wherein the PET polymers and/or BHT and ethanediol are recovered in step (d) by filtration.
16. The process of claim 15, wherein the filtration is high pressure filtration.
17. The process according to claim 16, wherein the filtration includes the addition of activated carbon or a combination of activated carbon and activated clay.
18. A process for removing contaminants from polyethylene terephthalate ("PET") components by depolymerising PET, including the following steps:
  - (a) transesterifying the material containing PET by reacting an alkanediol or alkanediols at a temperature below the boiling point of ethanediol with the material for a predetermined period of time to form a mixture containing embrittled PET;
  - (b) crushing the mixture and separating uncrushed material from the crushed material which contains PET;
  - (c) hydrolysing the crushed PET at elevated pressure and temperature for a predetermined period of time to form an ethanediol solution and crystals of terephthalic acid;

- (d) esterifying the ethanediol solution and crystals of terephthalic acid to form short chain PET polymers and/or bis (hydroxy ethyl) terephthalate ester ("BHT"); and
  - (e) recovering short chain PET polymers and/or BHT from the mixture.
- 5 19. The process of claim 18, wherein the alkanediol or alkanediols are selected from the group including ethanediol, 1:4 butanediol and 1:6 hexanediol and mixtures thereof.
20. The process of claim 18, wherein the alkanediol is ethanediol.
- 10 21. The process of any one of claims 18 to 21, wherein step (a) is carried out at a temperature in the range of 130 degrees Celsius and within 10 degrees of the boiling point of ethanediol .
22. The process of any one of claims 18 to 21, wherein step (a) is carried out at a temperature in the range of between 140 degrees Celsius and 160 degrees Celsius.
- 15 23. The process of any one of claims 18 to 22, wherein the uncrushed material includes poly vinyl chloride.
24. The process of any one of claims 18 to 23, wherein the predetermined period of time in step (a) is between 30 minutes and 120 minutes.
25. The process of any one of claims 18 to 23, wherein the predetermined period of time in step (a) is between 45 minutes and 60 minutes.
- 20 26. The process of any one of claims 18 to 25, wherein step (a) further includes the addition of a transesterification catalyst.
27. The process of claim 27, wherein the transesterification catalyst is selected from the group including antimony (III) oxide, antimony (III) acetate, germanium dioxide, manganese acetate, tetra butoxy titanium and mixtures thereof.
- 25 28. The process of any one of claims 18 to 27, wherein the PET is crushed to a size of less than 1 millimetre.
29. The process of any one of claims 18 to 28, wherein the PET polymers and/or BHT are recovered in step (e) by filtration.
30. The process of claim 29, wherein the filtration is high pressure filtration.
- 30 31. The process according to claim 30, wherein the filtration includes the addition of activated carbon or a combination of activated carbon and activated clay.
32. A process for recycling polyethylene terephthalate ("PET") from sources of used PET, including the steps of any one of claims 1 to 31.

33. Short chain PET polymers and/or BHT when recovered according to the process of any one of claims 18 to 31.
34. A process for separating polyethylene terephthalate ("PET") components from other materials, including the following steps:
- 5 (a) transesterifying material containing PET by reacting an alkanediol or alkanediols at a temperature below the boiling point of ethanediol with the material for a predetermined period of time to form a mixture containing embrittled PET; and
- 10 (b) crushing the mixture and separating uncrushed material from the crushed material which contains PET.
35. The process of claim 34, wherein the alkanediol or alkanediols are selected from the group including ethanediol, 1:4 butanediol and 1:6 hexanediol and mixtures thereof.
36. The process of claim 34, wherein the alkanediol is ethanediol.
- 15 37. The process of any one of claims 34 to 37, wherein step (a) is carried out at a temperature in the range of between 130 degrees Celsius and within 10 degrees Celsius of the boiling point of ethanediol.
38. The process of any one of claims 34 to 37, wherein step (a) is carried out at a temperature in the range of between 140 degrees Celsius and 160 degrees Celsius.
- 20 39. The process of any one of claims 34 to 38, wherein the uncrushed material includes poly vinyl chloride.
40. The process of any one of claims 34 to 39, wherein the predetermined period of time in step (a) is between 30 minutes and 120 minutes.
41. The process of any one of claims 34 to 39, wherein the predetermined period of time in step (a) is between 45 minutes and 60 minutes.
- 25 42. The process of any one of claims 34 to 41, wherein step (a) further includes the addition of a transesterification catalyst.
43. The process of claim 42, wherein the transesterification catalyst is selected from the group including antimony (III) oxide, antimony (III) acetate, germanium dioxide, manganese acetate, tetra butoxy titanium and mixtures thereof.
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| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>Int. Cl. <sup>6</sup> C08J 11/00, 11/04, 11/24; C08G 63/183<br>According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| <b>B. FIELDS SEARCHED</b><br><br>Minimum documentation searched (classification system followed by classification symbols)<br>IPC <sup>6</sup> C08J 11/00, 11/04, 11/24; C08G 63/183<br><br>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br>AU: IPC as above                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)<br>WPAT: IPC as above<br>JAPIO: IPC as above                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| Category *                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                           | Relevant to Claim No.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | GB 2123403, A (CELANESE MEXICANA SA) 1 February 1984<br>whole document                                                                                                                                                       | 1-43                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | US 5298530, A (GAMBLE et al.) 29 March 1994<br>whole document                                                                                                                                                                | 1-43                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | US 3776945, A (LIGORATI et al.) 4 December 1973<br>whole document                                                                                                                                                            | 1-43                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| <div style="display: flex; justify-content: space-between; align-items: center;"> <div style="display: flex; align-items: center;"> <input type="checkbox"/> Further documents are listed in the continuation of Box C.         </div> <div style="display: flex; align-items: center;"> <input checked="" type="checkbox"/> See patent family annex.         </div> </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 40%; vertical-align: top;">           * Special categories of cited documents :<br/><br/>           "A" document defining the general state of the art which is not considered to be of particular relevance<br/>           "E" earlier document but published on or after the international filing date<br/>           "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br/>           "O" document referring to an oral disclosure, use, exhibition or other means<br/>           "P" document published prior to the international filing date but later than the priority date claimed         </td> <td style="width: 10%; vertical-align: top; text-align: center;">           "T"<br/><br/>           "X"<br/><br/>           "Y"<br/><br/>           "&amp;"         </td> <td style="width: 50%; vertical-align: top;">           later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br/>           document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br/>           document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<br/>           document member of the same patent family         </td> </tr> </table> |                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | * Special categories of cited documents :<br><br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed | "T"<br><br>"X"<br><br>"Y"<br><br>"&" | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<br>document member of the same patent family |
| * Special categories of cited documents :<br><br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | "T"<br><br>"X"<br><br>"Y"<br><br>"&"                                                                                                                                                                                         | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<br>document member of the same patent family |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| Date of the actual completion of the international search<br>26 June 1995                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | Date of mailing of the international search report<br>5 JULY 1995 (05. 07. 95)                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| Name and mailing address of the ISA/AU<br><br>AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION<br>PO BOX 200<br>WODEN ACT 2606<br>AUSTRALIA<br><br>Facsimile No. 06 2853929                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | Authorized officer<br><br><div style="text-align: center;"> <br/> <b>H PHAM</b><br/>           Telephone No. (06) 2832293         </div> |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |

## INTERNATIONAL SEARCH REPORT

**Box I** Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international search report has not established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claim Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II** Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

PCT/AU 95/00201

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document<br>Cited in Search<br>Report |         | Patent Family Member |          |    |         |
|----------------------------------------------|---------|----------------------|----------|----|---------|
| US                                           | 5298530 | EP                   | 599309   | JP | 6211971 |
| US                                           | 3776945 | CA                   | 922050   | CH | 550753  |
|                                              |         | FR                   | 2116056  | GB | 1334558 |
|                                              |         | NL                   | 7116080  | YU | 33894   |
| DE                                           | 2158560 | JP                   | 54003857 |    |         |
| GB                                           | 2123403 |                      |          |    |         |
| END OF ANNEX                                 |         |                      |          |    |         |